Density-Functional Study of Magnetism in δ-Pu and Its Alloys

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At atmospheric pressure plutonium metal exhibits six crystal structures upon heating from room temperature to its melting point of 913 K. Among these phases, the δ-Pu has received a significant interest in the metallurgical community because of its high ductility that makes it easy to machine and form. The pure Pu δ phase is stable at elevated temperatures, between 593 K and 736 K, however a small amount of so-called δ-stabilizer, for example, Al, Ga, Zn, Cd, Zr, Sc, Am, Ce, In, or Tl can help to retain δ-Pu down to ambient temperature. In recent papers [1, 2] we proposed that δ-Pu is a disordered magnet that becomes unstable below about 600 K due to the antiferromagnetic (AF) ordering followed by a mechanical instability of the FCC phase. In this paper we study the effect of alloying on the magnetic properties of δ-Pu and the stability of the FCC phase.

There were several recent attempts to calculate electronic structure of Pu-based alloys. Becker *et al.* [3-5] have performed all electron full potential linear muffin-tin orbitals (FPLMTO) calculations of the electronic structure of Pu compounds (*Pu₃X*) with group-IIIB metals (X = Al, Ga, In and Tl). It is well known [6] that *X*-saturated δ-phase alloys forms two phase equilibrium with a *Pu₃X* compound that is isostructural to the Cu₃Au (*LI₂*) structure and the stability of the δ phase depends upon stability of this compound. These calculations failed severely to reproduce the equilibrium lattice parameter of the Cu₃Au-type compounds resulting in so-called overbonding and overly

large density. Moreover, the calculated formation energies of Pu_3In and Pu_3Tl compounds appear to be positive which does not correspond the reality. In order to improve results of these calculations Turchi *et al.* [7] used the phenomenological LDA+U method exploiting the idea of the partially localized *f*-electrons in the δ phase. Recently Harrison [8] used the empty-core pseudopotentials in order to predict the properties of actinide alloys. Though some interesting results were obtained, this approach remains semi-phenomenological and requires adjusting of the pseuodopotential parameters.

As was mentioned earlier [1], density functional theory (DFT) predicts a spontaneous formation of an ordered (AF) spin moment alignment in δ-Pu at T = 0K. Energetically very competitive is a disordered magnetic structure that represents a paramagnetic (PM) state of δ-Pu [2]. Fig. 1 shows KKR-ASA total energies of δ-Pu as a function of volume for AF and PM configurations. The energy difference between equilibrium PM and FM spin configurations is equal to 2.54 mRy/at. As was mentioned in paper [2], this small energy difference is not sufficient to rule out either magnetic configuration and spin entropy strongly favors the disordered magnetic structure at higher temperatures. As can be also found from Fig. 1, the disordered magnetic structure, that represents a PM state for δ-Pu, becomes the state with the lowest energy when the Wigner-Seitz radius (R_{WS}) expands beyond the equilibrium value (3.435 a.u.) approximately on ~ 6.3 %. This observation gives us some clue how doping Pu with larger solute atom could low the total energy of the PM phase with respect to the AF one and thereby stabilizing δ-Pu to lower temperatures.

Fig. 2.a. shows the energy difference between equilibrium PM and FM spin configurations of $Pu_{90}X_{10}$ disordered FCC alloys, where X = Sc, In, Ce, Tl, Am, Cm, Th,

and Ac corresponds to the elements that size exceeds the size of δ-Pu. As one can see all these elements promote stabilization of δ-Pu. Fig. 2.b. shows the energy difference between equilibrium PM and FM spin configurations of $Pu_{90}X_{10}$ disordered FCC alloys, where X = Ni, Co, Fe, Mn, Zn, Ga, Al, Cd, and In corresponds to the elements that size is smaller than size of δ-Pu. One can see that non-magnetic metals (Zn, Ga, Al, Cd, and Zr) also promote stabilization of δ-Pu. On the other hand, magnetic $3d$ transition metals (Co, Fe and Mn) destabilize δ-Pu

Fig. 3 shows the difference between PM and AF energies for $Pu_{90}X_{10}$ disordered FCC alloys as function of equilibrium volume for PM phase. One can see that position of $5f$-elements (Ce, Am, Cu, Th, and Ac) fits the line that corresponds to the energy difference between equilibrium PM and FM spin configurations of δ-Pu (see Fig. 1).

Table 1 show calculated equilibrium atomic volume (V), bulk modulus (B) and formation energy (ΔE^f) of PM $Pu_{75}X_{25}$ FCC solid solutions as well as PM Pu_3X ($L1_2$) compounds (X = Al, Ga, In and Tl). For comparison, we also show the experimental data available as well as results of previous calculations (Ref. [3]). For the first time, calculated densities of Pu_3X ($L1_2$) compounds match the experimental data very well. Our calculations show that formation of the Pu_3X ($L1_2$) ordered compounds is more favorable than formation of the disordered $Pu_{75}X_{25}$ FCC solid solutions.
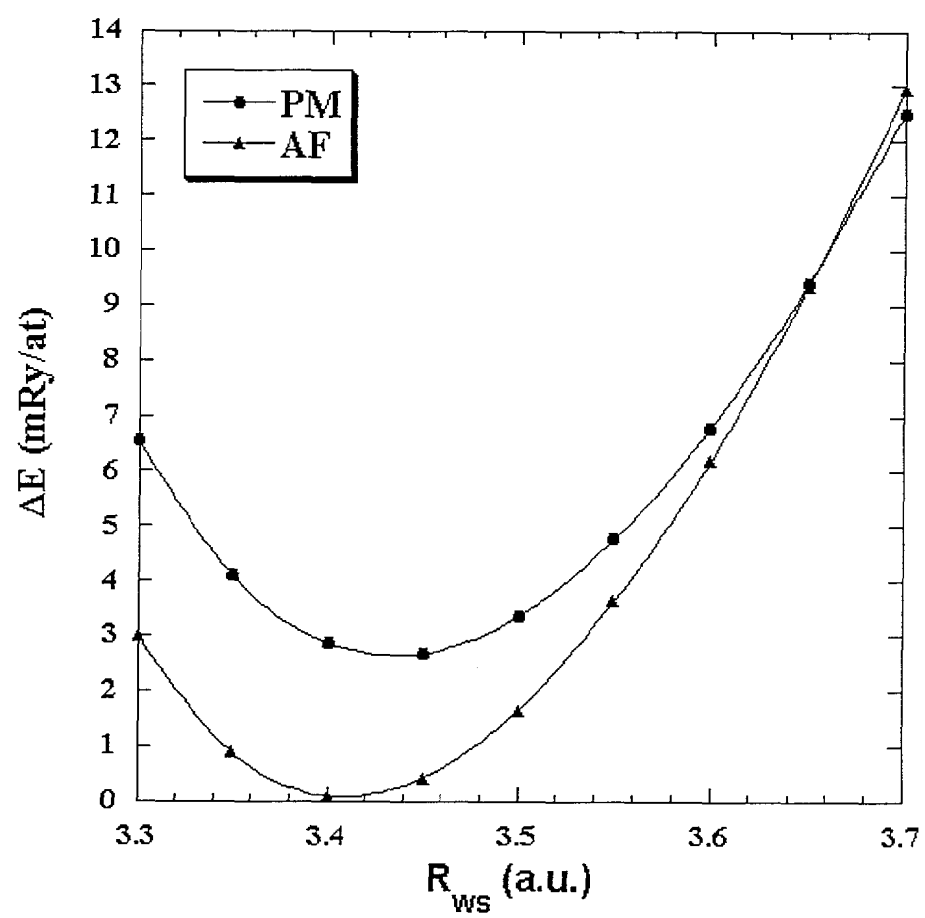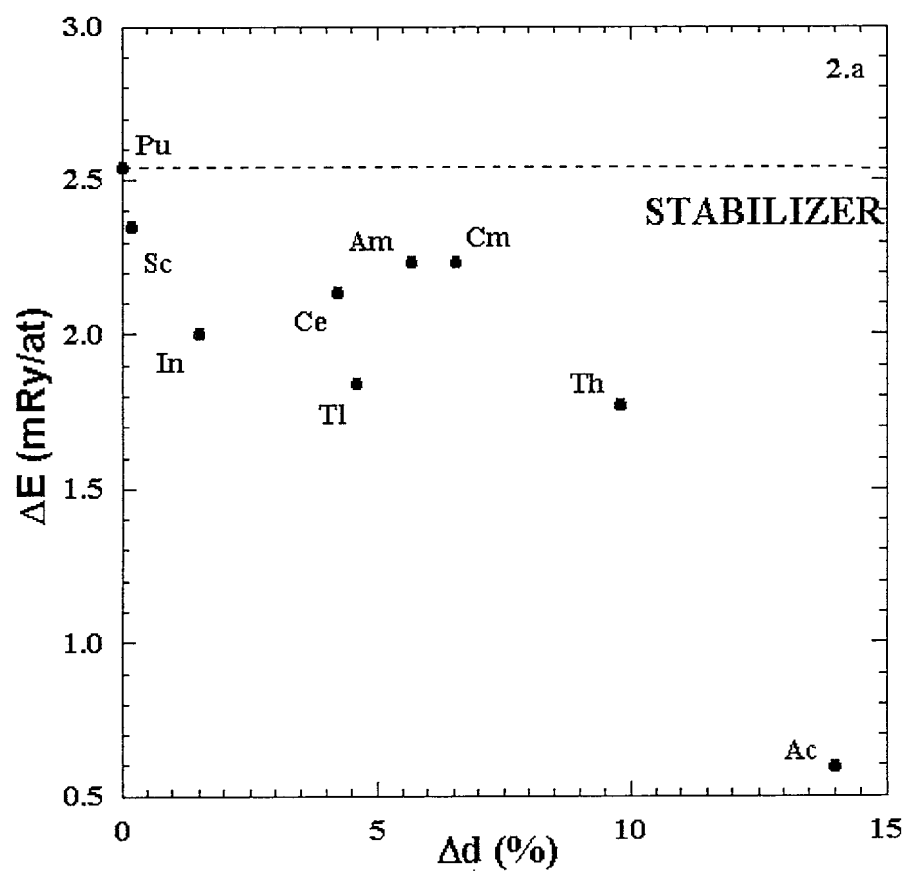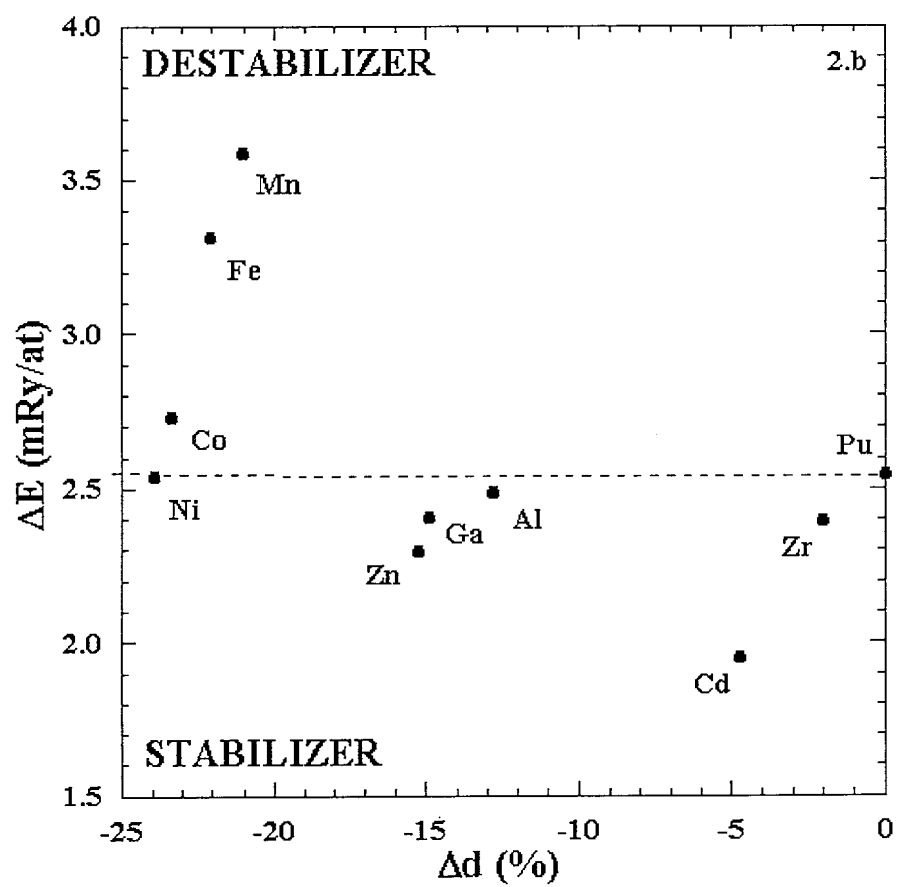
Figure 1.

Figure 2.a.

Figure 2.b.
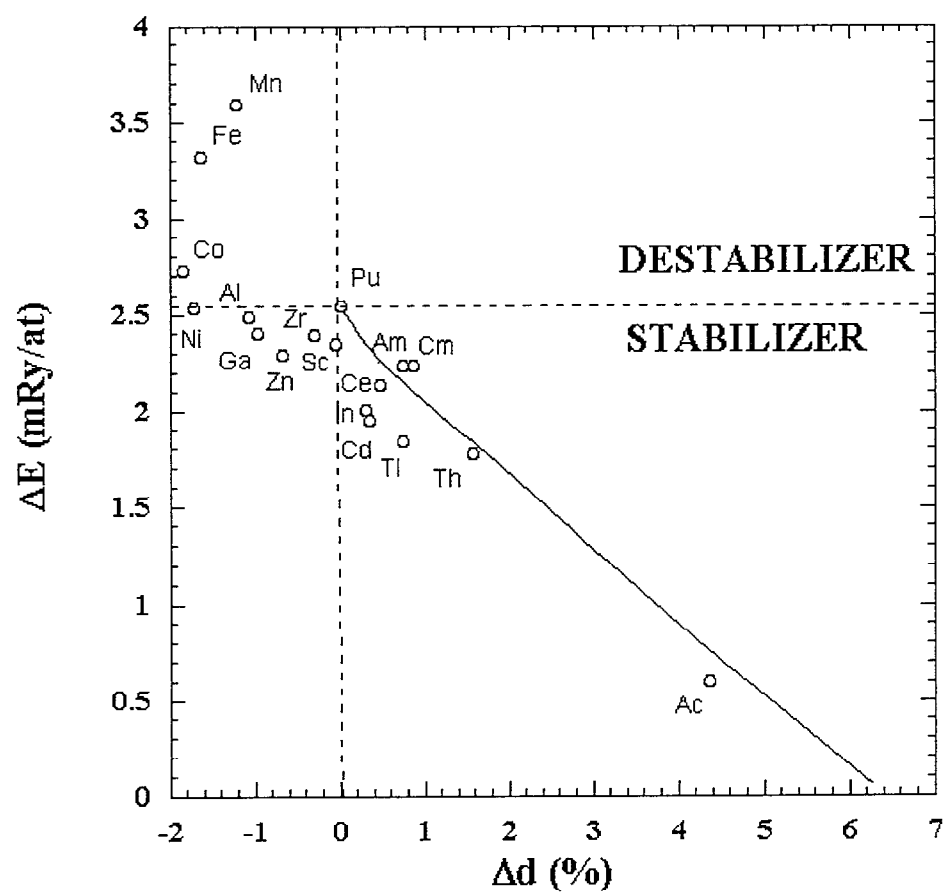
Figure 3.

Table 1.a

System	$V_{theor.}$ (Å^3)	$V_{exper.}$ (Å^3)	$V_{theor.}$ (Å^3)[3]	B_{theor} (GPa)	ΔE^f (mRy/at)
$Pu_{75}Al_{25}$	23.3			46.9	+ 7.22
Pu_3Al	23.2	23.0 [9]	17.6	50.7	- 4.16

Table 1.b

System	$V_{theor.}$ (Å^3)	$V_{exper.}$ (Å^3)	$V_{theor.}$ (Å^3)[3]	B_{theor} (GPa)	ΔE^f (mRy/at)
$Pu_{75}Ga_{25}$	23.5			45.5	+ 5.51
Pu_3Ga	23.0	22.6 [10]	17.6	52.6	- 10.93

Table 1.c

System	$V_{theor.}$ (Å^3)	$V_{exper.}$ (Å^3)	$V_{theor.}$ (Å^3)[3]	B_{theor} (GPa)	ΔE^f (mRy/at)
$Pu_{75}In_{25}$	25.6			44.4	- 0.25
Pu_3In	25.7	26.0 [11]	20.8	48.7	- 7.43

Table 1.d

System	V_{theor} (Å^3)	V_{exper} (Å^3)	V_{theor} (Å^3)[3]	B_{theor} (GPa)	ΔE^f (mRy/at)
$Pu_{75}Tl_{25}$	26.4			42.4	+ 5.36
Pu_3Tl	26.4	26.3 [12]	21.2	47.7	- 1.63

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